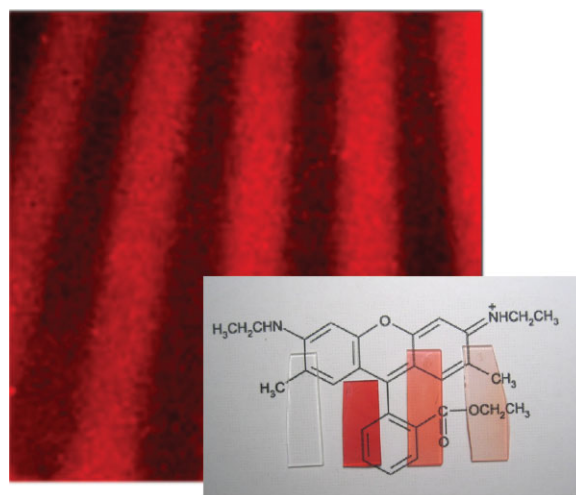


Luminescent and Optical Properties of Nanocomposite Thin Films Deposited by Remote Plasma Polymerization of Rhodamine 6G

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Mechanically stable and insoluble fluorescent thin films have been deposited by sublimating Rhodamine 6G laser dye in the downstream region of a low-power microwave ECR plasma using an experimental set-up designed to control the interaction of the dye molecule with the glow discharge. The use of reactive organosilane plasmas allows to control the dye distribution inside the matrix, leading to solid nanocomposite thin films containing non-aggregated dye molecules. The suppression of aggregates is a key issue to avoid fluorescence quenching. The obtained nanocomposite films are interesting because of their strong absorption and high fluorescence emission. In addition, they can be patterned using in situ plasma treatments in order to produce optically functional devices.



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Introduction

Plasma-enhanced chemical vapor deposition (PECVD) and plasma polymerization are well known techniques developed during the last decades for the deposition of thin films of oxides, polymers, metals, etc., as well as for the treatment of surfaces.^[1–4] When an organic precursor is introduced in a plasma, the precursor is fragmented, yielding neutral and charged molecular fragments and atomic species that usually produce highly cross-linked layers without retention of the monomer functionalities.^[1–4] Fostered for a wide

range of novel applications, the interest of the plasma deposition processes has changed during the last years towards the deposition of less cross-linked materials or of highly functionalized films retaining partially the chemical functionalities of the monomer molecules.^[5–8] In this regard, only a few papers in the bibliography have studied the plasma polymerization of dye molecules in parallel plate radiofrequency reactors,^[9–11] or the use of plasma to sublimate dye molecules.^[12] Very recently, we have described a new methodology for the fabrication of dye containing plasma nanocomposites by using remote microwave (MW) discharges.^[13,14] By this synthetic procedure, is it possible to obtain in one step colored and fluorescent nanocomposite thin films by the partial polymerization of Rhodamine 6G (Rh6G) laser dyes in a remote plasma. The main objective of this methodology is to retain not only the chemical functionalities present in the precursor, but a percentage of integer and non-aggregated Rh6G molecules embedded in the thin films in order to obtain highly luminescent nanocomposites.

Rh6G is a xanthen derivative used as gain medium in dye lasers.^[15,16] The Rh6G exhibits a strong absorption in the range ≈ 500 – 550 nm and a fluorescence quantum yield close to unity.^[16] In recent years, an increasing number of authors have studied the incorporation of Rh6G in inorganic and organic matrices for application in fields such as solid-state lasing, optoelectronics, optical filters, etc.^[17–23] The aggregation of the dye molecules is the main problem when trying to incorporate a high concentration of Rh6G as guest molecules in solids host materials prepared by sol-gel methods.^[17–21] This is because the Rh6G aggregates suppress the fluorescence of the rhodamine molecules.^[17–19,24,25] This phenomenon is especially important in solid films and can be observed in aqueous and alcoholic solutions of this molecule at relatively low concentrations.^[18] Different chemical synthetic strategies, such as the incorporation of the dye into mesostructured layers or porous gels, have been developed to decrease the percentage of aggregates and increase the fluorescence emission.^[17–19,21,23] For example, Rh6G-doped sol/gel mesostructured silica waveguides have shown amplified laser emission at pumping thresholds as low as $10 \text{ kW} \cdot \text{cm}^{-2}$.^[17]

In this paper, we present a complete study of the properties of Rh6G containing nanocomposite plasma polymeric thin films. The control of the interaction of the molecules with the plasma is used to obtain insoluble thin films with incorporated integer dye molecules and also to achieve the molecular dispersion of the dye within the solid matrix to enhance its luminescent properties.

Experimental Part

The electron cyclotron resonance (ECR) plasma reactor used for the synthesis of the thin films has a “downstream” configuration

operating at 100 W microwave power. The MW signal was applied to the plasma chamber through a flat Pyrex window. The plasma chamber was connected to the deposition chamber by standard CF ISO flanges. The gas pressure in the system was controlled by an adaptative pressure controller (VAT) connected to a capacitance pressure controller (Baratron). Argon and Tetramethylsilane (TMS, Aldrich) were dosed into the reactor using calibrated mass flow controllers (MKS). One side polished Si (100) wafers, quartz and glass slides were used as substrates in the deposition chamber. Rhodamine 6G (Aldrich) was sublimated inside the deposition chamber from a home-made Knudsen cell.

Fourier-transform infrared (FT-IR) spectra were collected in transmission and reflection in a Jasco FT-IR-6300 spectrometer for samples deposited on Si(100) and gold coated Si(100) $1 \times 1 \text{ cm}^2$ pieces, respectively. The films used for this analysis were thicker (300–500 nm) than for the rest of the experiments. This was necessary to ensure a sufficient intensity of the infrared bands.

X-ray photoelectron spectroscopy (XPS) spectra were acquired with a VG Escalab 210 photoelectron spectrometer operating at constant pass energy with a value of 20 eV. Non-monochromatized Mg K_{α} radiation was used as excitation source. Atomic ratios and surface concentrations were quantitatively determined from the area of the C 1s, N 1s, O 1s and Si 2p peaks. A Shirley-type background was subtracted and the peak areas were corrected by the electron escape depth, the spectrometer transmission function and the photoelectron cross-sections.^[26]

UV-vis spectra were recorded in a Perkin-Elmer $\lambda 12$ spectrophotometer for samples deposited in glass and quartz (fused silica) slides.

Fluorescence and photoluminescence excitation spectra (PLE) were measured in a Jobin-Yvon Fluorolog-3 spectrofluorometer using grids of 2 and 3 nm for the excitation and emission, respectively. The samples were deposited on non-fluorescent fused silica slides. The fluorescence spectrum was excited with radiation of 500 nm and the excitation was measured at 600 nm. Fluorescence microscopy images have been obtained with a Leica TCS SP2 confocal fluorescence microscope.

Non-contact Atomic force microscopy (AFM) measurements were carried out with a Cervantes AFM system from Nanotec using commercial non-contact AFM tips from Nanosensors. The images were processed using the WSxM software from Nanotec.^[27]

Field emission scanning electron microscopy (FESEM) measurements were obtained with a Hitachi Field Emission S-5200 Microscope for samples deposited on Si(100).

The films thicknesses have been measured with a Mahr Surf XC-10 profilometer, cross-sectional FESEM microscopy and by spectroscopic ellipsometry.

The optical properties of the thin films deposited on Si(100) have been measured with a variable angle spectroscopic ellipsometer (VASE) from J. A. Woollam Co., Inc. The analyzed spectral range was 250–2100 nm and the measurements were performed at incidence angles of 60, 65 and 70°. Depolarization and transmission measurements were additionally carried out.

Solubility of the samples have been tested comparing the UV-vis and microstructure of selected samples before and after immersion in a stirred deionized water bath at 318 K for 15 min.

Results and Discussion

Deposition of Colored Thin Films

A remote plasma reactor has been designed and optimized for the deposition of functionalized organic films by controlling the interaction of the growing film with the plasma during deposition. A scheme of this experimental set-up can be founded elsewhere.^[28] The distance (z) between the sample holder and the plasma can be modified during the deposition. The dye is sublimated in the downstream region from two Knudsen cells simultaneously to ensure homogeneous film growth over a wide area ($\approx 10 \text{ cm}^2$). The growth rate is controlled in situ by means of a quartz crystal monitor located very close to the sample holder and in the same plane. The dye is sublimated and condensed in the sample holder. During the deposition process, the molecules interact with the plasma species (i.e., radicals, ions, molecules, atoms and electrons) being partially fragmented and/or chemically modified. In addition, the plasma also activates the substrate surface.^[1–5] Our results indicate that in the downstream region it is possible to control effectively the interaction of the sublimated molecules and the plasma to avoid the complete fragmentation of the Rh6G molecules in the growing film (i.e. the deposition of dye-containing thin films). There are many parameters that influence this process; among these the most important are the MW power, the total pressure and gas composition, the distance (z) between the plasma and the growing film. Inert (Ar) or reactive (TMS/Ar mixture) MW plasmas have been used for the experiments, R being the ratio (mass flow of TMS)/(mass flow Ar). The downstream plasma polymerization of TMS precursor, in the absence of dye evaporation, yields transparent $\text{SiO}_x\text{C}_y\text{H}_z$ thin films^[3,29] with a growth rate of $\approx 8 \text{ nm} \cdot \text{min}^{-1}$ for $R=1.5$. The dependence of the film properties with these experimental parameters has been systematically studied in order to optimize the optical and luminescent properties of the films. A complete study of the correlations obtained is far from the objectives of this paper, and therefore we will present only some examples corresponding to the optimum deposition conditions.

The absorption spectra of Rh6G in aqueous and alcoholic solutions,^[30] colloids suspensions,^[31] or in dye doped films^[18,19,24,25] are typically characterized by an absorption maxima between 525 and 540 nm and a high energy shoulder. It is commonly accepted that the main absorption peak, at low energy, corresponds to the absorption by the free Rh6G monomer.^[18,19,24,25,30,31] The position of this maximum varies with the microenvironment of the dye molecule in each system.^[17,20,24,31] The high energy shoulder corresponds to light absorption by Rh6G dimmers and higher aggregates.^[18–21,24,25,31] Figure 1a shows the

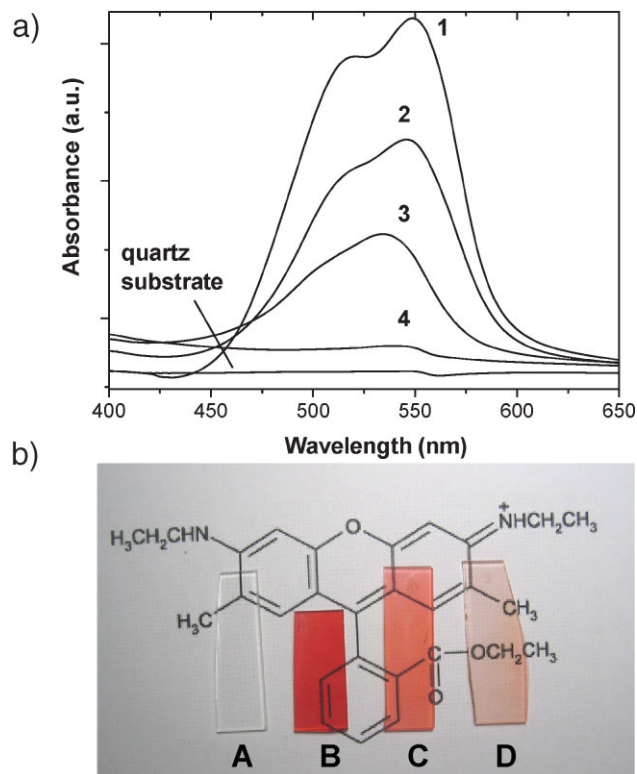


Figure 1. a) UV-vis spectra of plasma polymers as a function of the distance z between the sample holder and the plasma zone; b) Images of several plasma polymerized films deposited for different R values keeping the rest of the deposition parameter constant ($z = 5 \text{ cm}$, MW Power = 150 W and $P = 3 \times 10^{-2} \text{ mbar}$). Sample A: Quartz substrate, sample B: $R = 0$, sample C: $R = 1.5$, sample D: $R = 1.8$. The film thicknesses are $\approx 90 \text{ nm}$.

absorption UV-vis spectra of a series of $\approx 90 \text{ nm}$ thick films prepared under different experimental conditions, but setting the same experimental parameters in the spectrometer (i.e. unnormalized spectra). Sample 1 corresponds to a Rh6G film sublimated at $z = 20 \text{ cm}$ from the plasma zone. The spectrum is identical to a Rh6G film sublimated at the same pressure in the absence of the plasma (not shown) indicating that, from the point of view of the optical properties, the interaction of the dye molecules with the plasma is not significant under these conditions. Very different is the case of the films 2, 3 and 4 where a decrease in the light absorption is clearly seen in the spectra (Figure 1). These films have been obtained for $z = 10 \text{ cm}$ (sample 2) and $z = 5 \text{ cm}$ (sample 3). A pressure of $3 \times 10^{-2} \text{ mbar}$ and 100 W of MW power have been used during the synthesis of samples 1, 2 and 3. For comparison, the spectrum of sample 4, obtained at the same pressure but using 200 W of MW power and $z = 2 \text{ cm}$, is included in Figure 1. This sample depicted a yellowish color and did not show the absorption maxima at $\approx 550 \text{ nm}$ observed for the rest of the films.

Figure 1a illustrates the possibility of regulating the optical properties of the films as a function of the deposition conditions. To a first approximation we attribute the observed differences in the adsorption spectra to the dye molecule fragmentation degree. Samples 1 and 4 would depict minimum and maximum fragmentation degrees, respectively. The lack of light absorption at ≈ 520 nm in sample 4 indicates the absence of non-fragmented Rh6G molecules in the film. Although the partial fragmentation of the Rh6G produces a relatively decrease in the light absorption (i.e., samples 1 to 3 in Figure 1a), the plasma polymeric films show an intense color as it can be observed in sample B in Figure 1b.

Beside the z value, other parameters like the MW power and the gas pressure also affect the properties of the film and have to be thoroughly controlled and optimized. Our results indicate that the variation of the gas pressure has an effect similar to the variation of z . Thus, an increase in the dye fragmentation and polymer cross-linking is observed as the pressure decreases. At relatively high gas pressures ($>5 \times 10^{-2}$ mbar), the films exhibit an absorption spectrum very similar to those of the sublimated Rh6G films.

Figure 2a and b show two cross-sectional scanning electron microscopy (SEM) images of a sublimated Rh6G films and plasma polymerized thin films, respectively. Both films have been stored in air for 6 months after deposition. The sublimated film are composed of dye crystallites weakly adhered to the Si(100) surface and whose morphology and size change with the time. In contrast, the polymeric film presents a homogeneous and compact microstructure. In fact, normal SEM images of the polymeric films do not show any contrast observable by this technique. It is interesting to indicate that a similar compact microstructure is observed in all the plasma polymeric films deposited under different experimental conditions. An analysis of the morphology of these materials by AFM is included in a next section.

The normalized absorption spectra of another set of selected nanocomposite thin films of ≈ 90 nm thickness have been plotted in Figure 3a. In this experiment, we want to analyze the effect of the copolymerization of the sublimated dye with TMS. These films are obtained by using 100 W of MW power at 3×10^{-2} mbar and $z = 5$ cm for different R ratios. For comparison, the spectrum of the sublimated Rh6G film of similar thickness is also shown. In the spectrum of the sublimated Rh6G film, two absorption features at ≈ 550 and ≈ 515 nm, corresponding to the monomer and aggregates, are clearly visible. In comparison, the spectra of the plasma polymerized Rh6G film ($R = 0$) and the copolymerized films ($R > 0$) are very different from that of the evaporated one. The intensities of the high energy shoulders, and the full width at half maximum (FWHM) of the absorption peaks (Figure 3b)

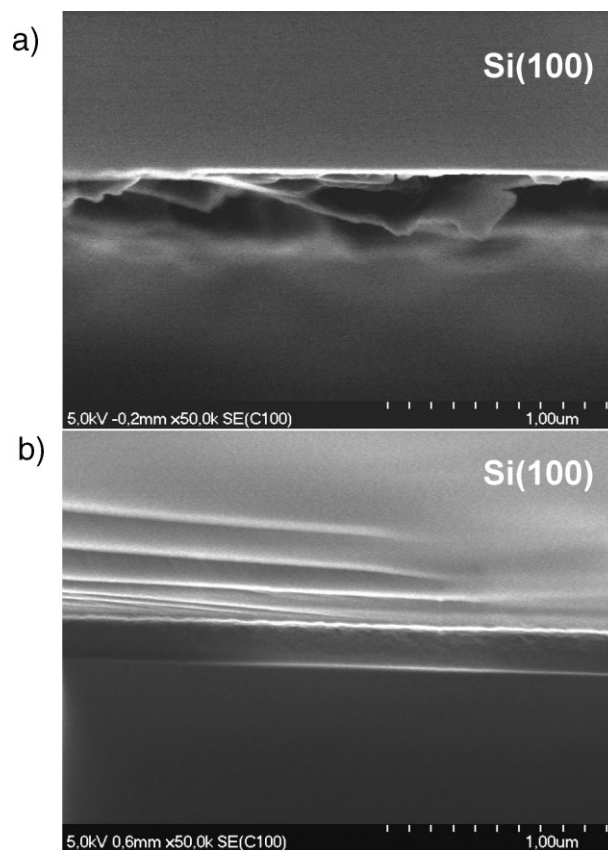


Figure 2. Cross sectional SEM microscopy images of a) a vacuum sublimated Rh6G thin film, b) a plasma polymerized Rh6G thin film (100 W MW power, $P = 3 \times 10^{-2}$ mbar and $z = 5$ cm). Both layers are deposited onto Si(100) wafers. The films have been stored in air for six months before the measurements.

decrease dramatically as R increases. In fact, the absorption curve of the film synthesized at $R = 1.5$ shows a nearly symmetrical profile centered at ≈ 524 nm and a minimum FWHM of ≈ 55 nm. This analysis reveals that the interaction of the downstream TMS/Ar plasma with the sublimated Rh6G molecules produces an effective modification of the dye aggregation degree in the film. This process is particularly efficient in obtaining isolated Rh6G molecules for $R = 1.5$. The intensity of the light absorption decreases as R increases, as it can be seen in Figure 1b. However, it is interesting that the film deposited for $R = 1.5$ (sample C) is only slightly less absorbent than the film deposited for $R = 0$ (sample B).

Thin-Film Characterization

XPS survey spectra of a reference sublimated Rh6G film, and two plasma deposited films obtained for $R = 0$ and 1.5 have been represented in Figure 4. The surface composition determined by the XPS analysis is shown in Table 1.

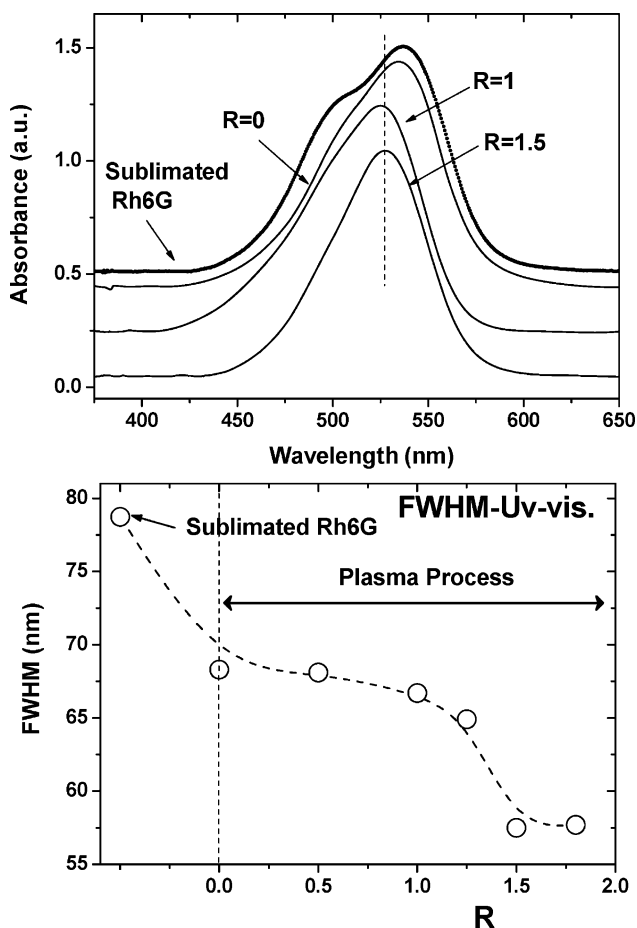


Figure 3. a) Normalized absorbance spectra of plasma polymerized thin films as a function of the R parameter. The curves have been vertically shifted for the sake of clarity. b) FWHM of the curves in a) as a function of R . The value corresponding to a sublimated film is included for comparison.

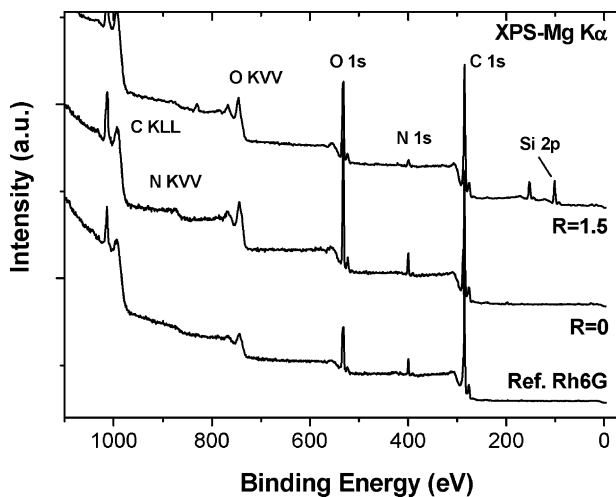


Figure 4. XPS Survey spectra of a reference sublimated sample and two films deposited for $R=0$ and 1.5.

Table 1. Atomic percentages of evaporated and two polymerized films compared with the percentages derived from the Rh6G formula.

	C	O	N	Si
	at.-%	at.-%	at.-%	at.-%
Sublimated Rh6G	79	15	6	–
$R=0$	68	26	6	–
$R=1.5$	68	19	3	10
Rh6G (formula)	85	9	6	–

The sublimated and plasma polymerized films for $R=0$ are composed of C, O and N atoms with atomic percentages that are close to those derived from the composition of the dye molecule. While both films are comparatively enriched in oxygen, the atomic oxygen percentage of the film deposited at $R=0$ is significantly higher. The oxygen enrichment is a general phenomenon in plasma polymerized organic thin films. The origin of this oxygen enrichment has been attributed to post-deposition reactions with air and/or direct incorporation of oxygen from the reactor during the deposition.^[1,3] The film deposited at $R=1.5$ shows a composition similar to the film deposited for $R=0$ with an additional Si percentage of ≈ 10 at.%. Additional details about the XPS analysis of sublimated and plasma polymerized films for $R=0$ and organosilicon thin films prepared in a similar reactor can be found elsewhere.^[13,28,29]

Bulk analysis of the Rh6G films has been carried out by FT-IR spectroscopy. Figure 5 shows the FT-IR spectra of an evaporated Rh6G and two polymeric layers deposited for $R=0$ and 1.5. The spectrum of the sublimated film shows

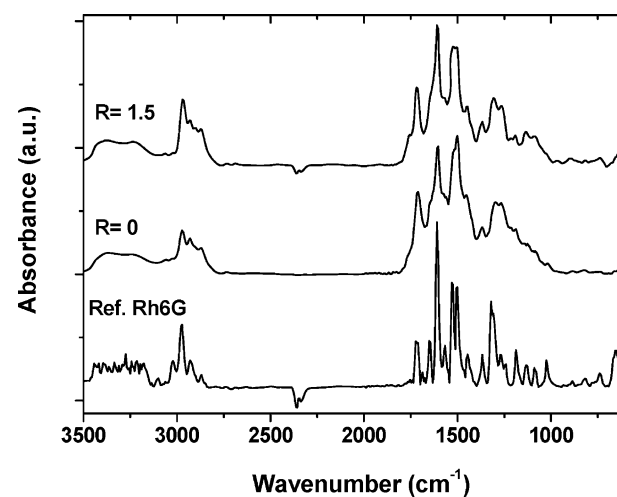


Figure 5. FT-IR absorption spectra of a plasma polymerized layer and two films deposited for $R=0$ and 1.5.

the vibrational bands corresponding to the Rh6G molecule that have been fully assigned by several authors.^[13,32,33] The most intense bands are: low intense features at 615–670 cm^{-1} assigned to C–C–C in plane bending, at 1215 cm^{-1} to C–O–C stretching, at 1115 cm^{-1} to C–H aromatic in plane bending, at 1140, 1165, 1210 cm^{-1} to C–H in plane bending and C–C stretching, at 1320, 1370, 1450 cm^{-1} associated with aromatic C–C and C–N stretching, at 1495, 1540 and 1630 cm^{-1} assigned to aromatic C–C stretching, at 1715 cm^{-1} attributed to C=O stretching vibration in the carbonyl phenyl group, a band at $\approx 2950 \text{ cm}^{-1}$ that can be attributed to C–H stretching vibrations, and the two weak bands at 3200 and 3390 cm^{-1} due to N–H vibrations. The FT-IR spectra of the plasma polymerized films ($R=0$ and 1.5) show less defined and broader features than those corresponding to the sublimated films at similar wavelengths. The most intense features correspond to aromatic and carbonyl stretching vibrations. This result reveals that original structural groups of the Rh6G molecule are incorporated in the polymeric films. The broadening of the IR bands is a typical effect in plasma polymers.^[1,3] Thus, the FT-IR spectrum features of the plasma thin films can be interpreted as the results of the cross-linking of the Rh6G molecules during the plasma deposition (i.e. extensive fragmentation of the dye molecule in the film), the complete or partial hindering of vibrational modes of the dye molecule confined in the cross-linked polymeric matrix and the incorporation of fragments of the dye molecule. A similar effect has been observed in dye-doped silica xerogels.^[32] The plasma polymer spectrum shows an additional wide and intense band at $\approx 3150\text{--}3450 \text{ cm}^{-1}$ due to O–H vibrations, a feature that is congruent with the increase in oxygen content shown by the XPS characterization.

The spectrum of the films deposited for $R=0$ and 1.5 are very similar. The latter shows an additional low intense band at $\approx 1075 \text{ cm}^{-1}$ that can be attributed to Si–O–Si stretching mode.^[3,29] In addition, the relatively higher intensity of the bands at $\approx 2950\text{--}2980 \text{ cm}^{-1}$ of this latter film very likely indicates an increment in the cross-linking of the polymeric structures due to higher dye fragmentation with respect to the film deposited for $R=0$. This process decreases the number of integer Rh6G molecules in the matrix what is congruent with the relative decrease in the color intensity observed as R increases for films of the same thickness (see samples B to D in Figure 1b).

The analysis of the deposited films shows clearly that the plasma produces partial fragmentation and cross-linking of the Rh6G molecules in the films. Both fragmented and isolated dye molecules contribute to the XPS and FT-IR spectra. The fragmentation process is congruent with the decrease in the light absorption and the increment in the fluorescence emission intensity

observed for the plasma polymerized thin films shown in the next sections, in comparison to the vacuum sublimated films of similar thicknesses.

Luminescent and Optical Properties

Normalized excitation and fluorescent emission spectra of three films deposited for $R=0, 1$ and 1.5 are shown in Figure 6. The excitation spectra have similar shapes to the corresponding absorption spectra shown in Figure 3a. The excitation peaks show maxima that shift from 539.5 to 523.0 nm as R increases. In addition, the peaks depict a shoulder at lower wavelength that decreases in intensity as R increases. The FWHM of these peaks varies from 79.5 to 60.0 nm as R decreases. The fluorescence emission maxima in Figure 5 are blue-shifted from 581.7 nm for $R=0$ to 554 nm for $R=1.5$. In addition, a reduction in the width of the signal is apparent as R increases. These spectral narrowing of the fluorescence and excitation spectra has been attributed by many authors to the suppression of dye-aggregation reported for Rh6G in

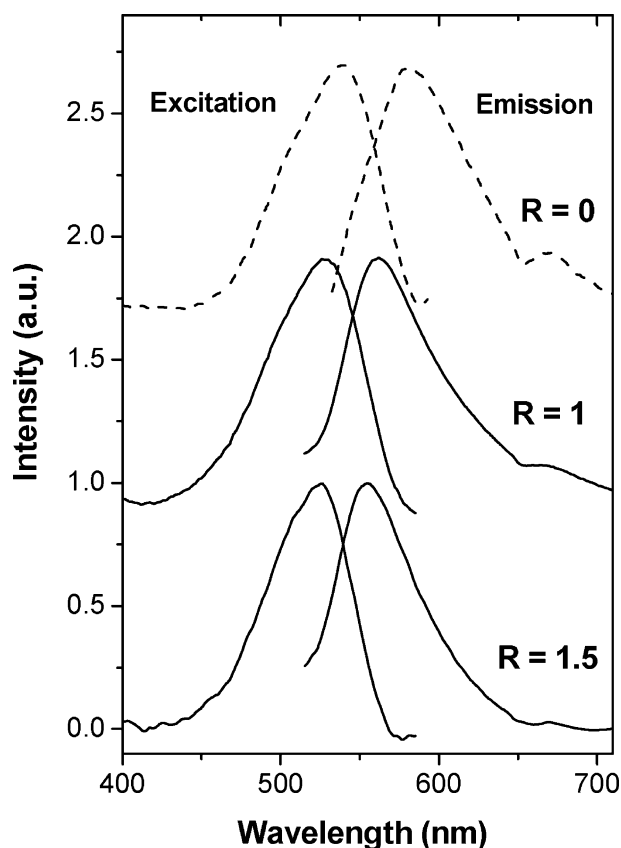


Figure 6. Normalized fluorescence excitation and emission spectra from three films deposited at $R=0, 1$ and 1.5. The excitation wavelength for the fluorescence is 500 nm. The excitation spectra have been measured at 600 nm.

alcoholic or water solutions or hosted in solid matrices.^[16,19,30]

The strong luminescent emission observed for films of less than 100 nm in thickness and the shape of the optical absorption spectra (cf. Figure 6) supports the presence of a high percentage of integer Rh6G molecules in the films. According to the common knowledge for the Rh6G molecule, the absorption-like behavior of the excitation spectra and the decrease in the FWHM of the excitation and fluorescence peaks as R increases must be related to the presence of a high percentage of non-aggregated Rh6G molecules in the films.^[18,19,30] Our experimental results indicate that the aggregation degree of the dye molecules in the solid films decreases mainly due to the reaction of TMS fragments with the dye aggregates during the synthesis. The XPS and FTIR analyses confirm that fragments of TMS have been effectively incorporated in the films. We can therefore assume that the films are formed by dye molecules within a solid matrix formed by the plasma polymerization of the dye ($R=0$) or by the copolymerization of the dye with TMS ($R>0$). The observed shifts in the absorption, excitation and emission maxima (Figure 3a and 6) can be attributed to changes in the chemical environment surrounding the dye molecule and to the decrease in the concentration of Rh6G molecules in the polymeric matrix as R increases.^[16,20]

All the results show that it is possible not only to prepare good quality colored films with this method, but also to control the chemistry of the plasma to get molecular dispersion of the dye inside of a solid matrix. It is interesting to stress that fragmentation and a partial destruction of the structure of a fraction of dye molecules in the films is necessary in order to optimize the properties of the layers. On one hand, the molecular fragmentation of the dye is required to produce a cross-linked matrix to embed the fraction of dye molecules that do not undergo this process. This furnishes mechanically stable and insoluble solid structures. On the other hand, the control of the partial dye fragmentation can be used to suppress the formation of dimmers and/or higher dye aggregates that influences the final luminescent properties of the nanocomposites. When the fragmentation degree is too high, the films do not present any absorption/fluorescence bands (cf. spectrum 4 in Figure 1a). It must be also stressed that the reactivity of the Rh6G molecules with the plasma ions and radicals coming from the fragmentation of the TMS molecule play also a key role for the control of the optical properties of

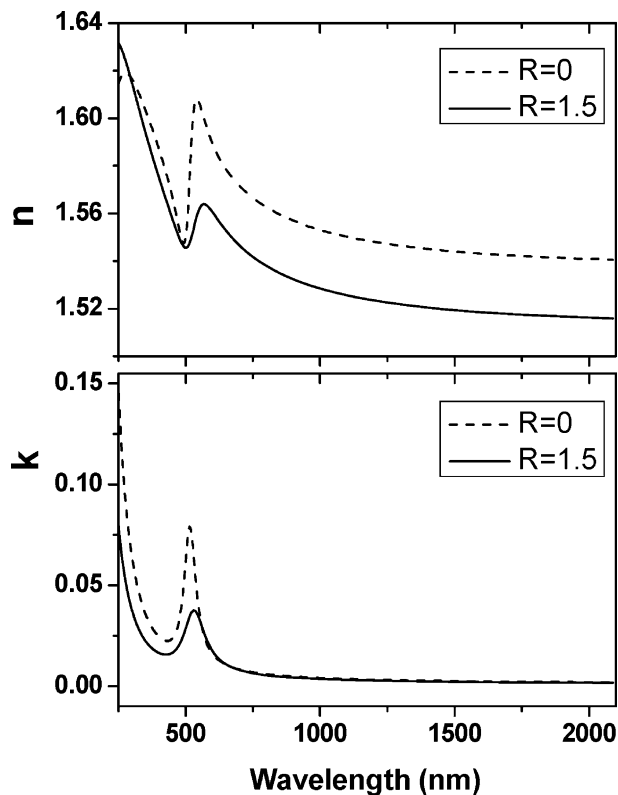


Figure 7. Refractive index n and extinction coefficient of two plasma polymeric thin films deposited for $R=0$ and 1.5

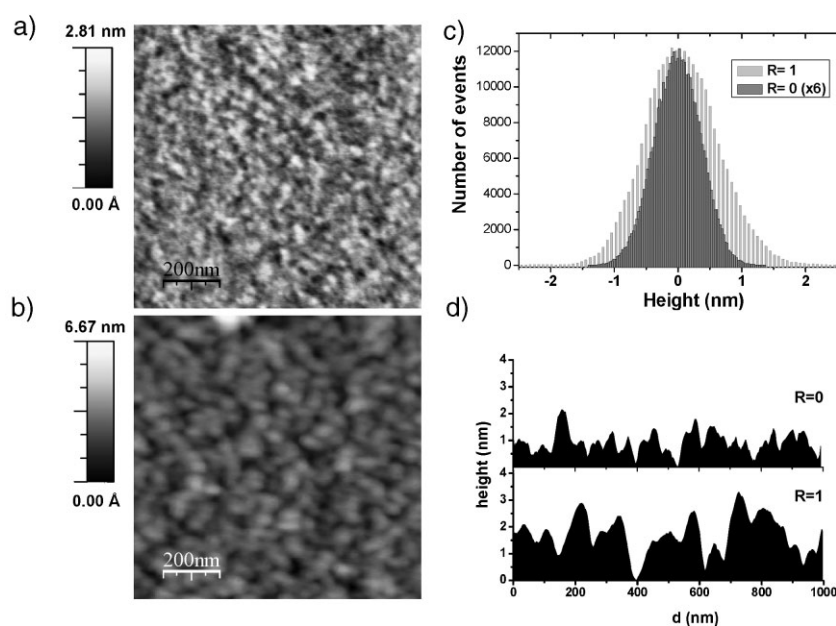


Figure 8. AFM tapping mode images ($1 \times 1 \mu\text{m}^2$) of plasma polymeric films, ≈ 100 nm thick, deposited for a) $R=0$, and b) $R=1$; c) Height distributions; d) Lines profiles for the two thin films

the nanocomposites. In fact, we attribute the success in preparing colored and fluorescent dye nanocomposites by this method to the control of this fragmentation process under remote plasma conditions. From a practical point of view, it is also interesting to note that no evolution of the absorption and fluorescent emission has been detected for films stored in air up to six months after deposition.

Besides the UV-vis spectral analysis, the study of the optical properties of the films has been performed by spectroscopic ellipsometry. The optical properties of the layers are well defined in all analyzed ranges. Figure 7 shows the complex refractive index curves corresponding to the films deposited for $R=0$ and 1.5. The extinction coefficient, k , decreases sharply for wavelengths longer than 560 nm (i.e., values above the absorption maxima). Thus, the films are transparent in the region corresponding to the fluorescence emission and at higher wavelengths, what is very interesting for optical applications. Besides, the n values decrease as R increases, indicating the possibility to adjust the optical properties of the films by controlling the layer composition. Thus, the n values at 632.8 nm are 1.58 and 1.55 for the samples deposited with $R=0$ and 1.5, respectively. This reduction in the n values as R increases is similar to the evolution observed in $\text{SiO}_x\text{C}_y\text{H}_z$ plasma films when the carbon content decreases.^[29] It is also similar to the general tendency observed in optical thin films where organic layers of amorphous carbon or polymeric films reached higher n values than silicone-like polymers.^[34] Both types of films present an important absorbance in the UV spectral region (i.e. for wavelengths lower than 400 nm).

Dye Morphology and Micropatterning by Plasma Etching

These materials are clear candidates for the fabrication of photonic and optical structures (i.e. photonic waveguides and optical sensors). For this type of applications, it is extremely important to synthesize smooth films that can be patterned by ion or plasma etching to produce devices. Therefore, as a feasibility study, we investigated the morphology of the film surfaces and performed a patterning of the films by O_2 -plasma etching.

The topography of the layers has been studied by non-contact atomic force microscopy (AFM). Figure 8a to c shows two AFM images, the corresponding size distributions and two line profiles for films of the same thickness (≈ 90 nm) obtained at $R=0$ and 1. The RMS roughness of these films is extremely low and increases slightly from 0.4 nm for $R=0$ to 0.6 nm for $R=1$. A very smooth Gaussian type distribution has been obtained from the roughness analysis included in Figure 8c. The distribution is 0.3 nm wider for the film corresponding to $R=1$. The

AFM images of the film obtained for $R > 0$ show (Figure 8b and c) the granular structure observed in silicone-like $\text{SiO}_x\text{C}_y\text{H}_z$ thin films prepared with similar plasma conditions.^[35] Thus, the AFM analysis shows that the films are extremely homogeneous and smooth, and are not formed by dye crystallites typical of evaporated dyes (see Figure 2). Another interesting characteristic is that they adhered well to the substrate. The difference between the surface morphology of the two investigated films reflects a different plasma interaction during the film synthesis in the presence or the absence of TMS in the discharge.

Figure 9a and b show scanning electron micrographs and fluorescence optical images of patterned plasma films obtained by post-deposition treatment of the films using O_2 -plasma with a tantalum shadow mask. For this purpose, the films were covered by the shadow masks and introduced again in the plasma reactor where they were etched during 15 min with an oxygen plasma excited with 300 W at 10^{-2} mbar. As it can be seen, the O_2 -plasma

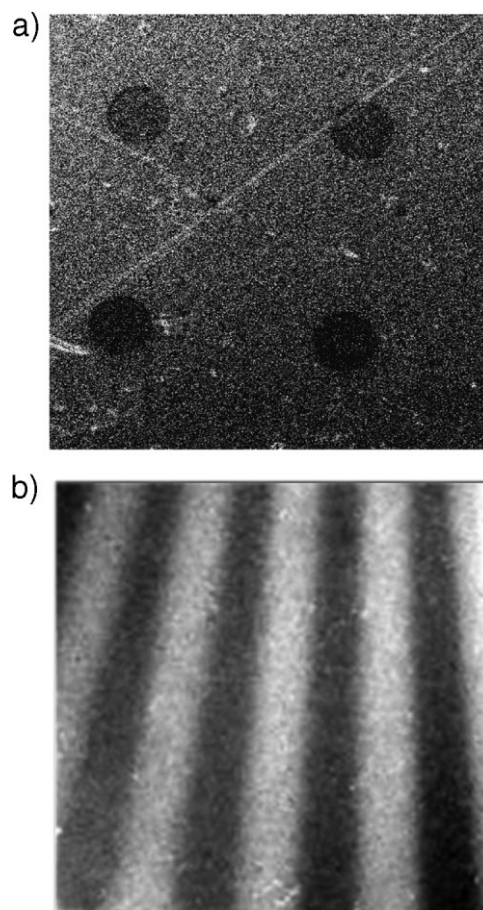


Figure 9. Fluorescence images recorded with a confocal fluorescence microscope for plasma Rh6G thin films of ≈ 100 nm thickness deposited for $R=1$ and subjected to an oxygen plasma etching through a Ta shadow mask: a) Circular patterns of $\approx 15 \mu\text{m}$ diameter, b) Patterns of $\approx 50 \mu\text{m}$ width.

etches very efficiently the exposed surface (i.e., the dark regions) of the films removing the film up to the substrate. The patterns are well defined and the non-exposed parts (i.e. the bright regions) have the same optical and luminescent properties than the original film. Although the walls of the generated structures are well defined on the scale accessible to the confocal fluorescence microscope, the etching process and the quality of the patterns can be easily improved by biasing the sample holder (i.e., extracting oxygen ions normal to the sample surface) during the etching process.^[2] The possibility of patterning the films by in situ treatments is a key property for the fabrication of microphotonic devices using this novel technology. The fabrication of devices using this process of deposition and etching will be further studied in future works.

Conclusion

The present paper shows that low energy remote MW plasmas can be applied to the synthesis of nanocomposite thin films containing complex molecular structures coming from the precursor molecules used. The results reported here on Rh6G laser dye molecules are a good example of such a possibility, particularly if we take into account that these compounds are very sensitive to molecular damages (i.e. the breaking of bonds or the opening of a ring producing the loss of the absorption and luminescent properties of the molecule). For $R=0$, the electron energy seems the main parameter controlling the polymerization degree of the films.^[26] However, when TMS is added to the discharge, the results show that the presence of reactive fragments of the organosilane molecule also contributes to the fragmentation of the dye. These fragments are incorporated into the growing films, modifying their composition, morphology and properties. The most remarkable achievement obtained by this procedure is the synthesis of highly luminescent thin films containing non-aggregated dye molecules. The experimental results indicate that this process is particularly efficient when a flow of TMS is added to the discharge at an optimum value of $R = 1.5$.

The method developed in this work permits to regulate the plasma interaction with the sublimated molecules, controlling the final structure and optical properties of the synthesized film or, eventually, to etch selected patterns of the deposited materials. The possibility of combining the deposition of dye containing films with the synthesis of other optical inorganic films (i.e., SiO_2 , $\text{SiO}_x\text{C}_y\text{H}_z$ and TiO_2 films) and nanostructured materials in the same reactor by changing the deposition conditions and precursors opens the way to the fabrication of complex photonic devices for different applications.^[35–37]

Among other, the following points can be quoted as advantages of this novel synthetic approach: 1) It is a general synthetic method applicable to other thermally stable dyes or complex molecules; 2) It provides a very high absorption-luminescence in films of several tens of nanometer due to the deposition of a high percentage of non-aggregated dye molecules; 3) It is a one-step solventless method compatible with the present silicon technology; 4) The films are mechanically stable and insoluble and their properties do not vary with time; and 5) It provides the possibility of processing the films by etching methods using masks and/or by integrating the film in multilayer structures.

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